HEAVY OIL UPGRADING USING HALIDE CATALYSTS
IN A BUBBLING MICROAUTOCLAVE

A. Chakma, E. Chornet, R.P. Overend
Université de Sherbrooke, Sherbrooke, Québec, Canada, J1K 2R1

and

W. Dawson
Energy Research Laboratories, CANMET, Ottawa, Ontario, Canada, K1A 0G1

ABSTRACT

Athabasca bitumen has been treated with halide catalysts under a continuous flow of H_2 in a 15 mL microautoclave. The H_2 was bubbled through the liquid using a microporous steel grid. $ZnCl_2$, $CuCl$ and $ZnCl_2/CuCl$ mixtures, with and without tetralin, were used as catalysts. The experimental conditions were: 13.8 MPa operating pressure, 1 L_{STP}/min as H_2 flowrate, 425-450°C and 30 min as reaction temperature and time respectively. $ZnCl_2$ has been found effective for converting asphaltenes into maltenes while lowering the coke formation with respect to the uncatalyzed reaction. The addition of tetralin to the reaction mixture minimized coke and gas formation.

INTRODUCTION

Bitumen and heavy oil upgrading has been the subject of many investigations since the early thirties (1). Present industrial technologies such as delayed coking or fluid coking result in the formation of large amounts of coke (up to 22% of the feed) (2). This decreases the yield of valuable liquid products. Whereas coke derived from petroleum in general may find a variety of uses, the high sulphur content of the coke produced from Canadian oil sands bitumen such as Athabasca bitumen, precludes its use (3).

Hydrocracking of Athabasca bitumen has proven to yield 10-15% higher liquid distillate product than conventional coking processes (4). Catalysts are required for effective removal of sulphur and nitrogen and to improve liquid yields. Coke is also formed during hydrocracking, although

significantly less than in coking. However, this creates operational problems such as reactor fouling and catalyst poisoning. Coke formation increases with temperature (5,6) and decreases with hydrogen partial pressure (5). Addition of coal and coal-based catalysts has been claimed to reduce coke formation (7).

Coke formation from oil sands bitumen is believed to be related to its high asphaltene content (2). Dickie and Yen (8) have studied structures of asphaltenes from various sources and postulated that asphaltene aggregates are made of planar sheets of condensed aromatic rings, saturated carbon chains and a loose net of naphthenic rings. Therefore, polynuclear aromatic hydrocarbons may be considered as possible constituents of asphaltene and catalysts which are effective in hydrocracking polynuclear aromatic compounds should also be effective in asphaltene hydrocracking.

Molten halide salts have been found to be excellent catalysts in the hydrocracking of the polynuclear (9,10) and alkyl substituted polynuclear aromatic hydrocarbons (11). Zielke et al. (9) have shown the superiority of molten $ZnCl_2$ catalysts over conventional hydrocracking catalysts for pyrene, coal and coal extract and subsequently carried out continuous hydroliquefaction of subbituminous coal in molten $ZnCl_{2(12)}$.

Herrmann et al. (13) carried out a comparative study of Fe, $ZnCl_2$ and $ZnCl_2$-promoted Fe catalysts for hydrocracking of Athabasca bitumen. They found $ZnCl_2$ to be the most active, to produce less hydrocarbon gas and significantly less sulphur in the liquid product. Nomura et al. (2) studied hydrocracking of Athabasca asphaltene over molten $ZnCl_2$-KC1-NaCl mixtures with and without an additive of some transition metal chlorides and found a mixture of $ZnCl_2$-KC1-NaC1$_5$ to give higher asphaltene conversion (60% pentane soluble) and small amounts of coke (3.7% benzene insoluble). Based on this information we decided to carry out systematic experiments to investigate the hydrocracking of Athabasca bitumen with molten $ZnCl_2$, CuC1 and their mixtures with and without tetralin. This latter hydrogen donor compound was added to rapidly transfer H and then prevent coke formation by recondensation of the hydrocracked radicals.

FEEDSTOCK AND REAGENTS

Athabasca bitumen produced by hot water process from mined oil sands of the McMurray stratigraphic unit by Suncor Inc. and obtained from the Alberta Research Council was used as the feedstock. Table 1 summarizes the relevant properties of the bitumen.

All the reagents used were of ACS reagent grade. Tetralin and $ZnCl_2$ were purchased from Aldrich Chemicals, Milwaukee, WI.: CuCl was purchased from Anachemia Ltd., Montreal and hydrogen was purchased from Liquid Carbonic Inc., Montreal.

EQUIPMENT

Traditionally laboratory scale hydrocracking experiments have been carried out in stirred autoclaves (13) and rocking autoclaves (2). However, the fluidodynamic conditions in these traditional autoclaves are considerably different from those of an industrial hydrocracker because industrial hydrocrackers operate under continuous flow conditions.

To simulate industrial conditions as closely as possible we used a bubbling microautoclave system of our own design. A schematic diagram of the experimental setup is shown in Fig. 1. It consists of a 15 mL bubbling microautoclave, water cooled condenser, gas collection assembly, molten salt heating bath, cooling water bath, connecting tubings, and instrumentation. The bubbling microautoclave is the heart of the experimental setup and is equipped with a microporous steel grid, through which gas can be dispersed.

The gas collection assembly was specially designed to collect all the gases. It consists of two 75 L tanks, capable of withstanding pressures up to 20 psig. The contents can be mixed thoroughly by means of two built-in stirrers. In addition a pump can transfer the contents from one tank to another and vice versa thereby facilitating intermixing the contents of both.

EXPERIMENTAL PROCEDURE

The microautoclave was filled with about 7 g of bitumen for the non-catalytic experiments plus desired amounts of catalysts for the catalytic experiments. $ZnCl_2$ and $CuCl$ were oven dried at 100°C for about 3 h prior to use to eliminate any moisture. The microautoclave was then completely sealed. Hydrogen was then bubbled through the microporous grid and the system pressure was raised to the desired pressure (13.8 MPa). The hydrogen flowrate (1 L_{STP}/min) was established by a pre-calibrated mass flow meter (Brooks Instruments, Model 5850). The microautoclave was then plunged into the preheated molten salt bath heater and the previously evacuated gas collection assembly was started. The temperature of the microautoclave contents was monitored constantly by an electronic temperature indicator (Analogic, Model AN2572). It usually took about 5-7 min to reach the desired reaction temperature (425°-450°C). Experiments were carried out for 30 min after reaching the reaction temperature. The microautoclave temperature was carefully controlled as follows: when it exceeded the desired reaction temperature by 2°C, the autoclave was partially withdrawn momentarily from the molten salt bath to reduce the temperature to the reaction temperature. In this manner it was possible to stay within ±3°C of the desired temperature.

At the end of the experiment, the microautoclave is quickly immersed into the cooling water bath while the hydrogen is continued. When room temperature is reached (25°C), which takes about 1-2 min, the gas flow is stopped. The gas remaining in the system is then evacuated into the gas collection assembly.

ANALYTIC PROCEDURE

The gases were well mixed in the gas collection assembly for about 1 h, then analyzed by a gas chromatograph (Hewlett Packard, Model 5890) equipped with a Porapak Q and a Molecular Sieve column in series.

The microautoclave was weighed before and after the experiment and the difference gave the quantity of gas formed plus any entrainment. Usually entrainment was negligibe as the condenser was purposely overdesigned and was filled with metal springs. Most of the gases were thus condensed and returned to the microautoclave.

The microautoclave was then cleaned thoroughly with dichloromethane. Dichloromethane insoluble products were filtered, dried in an oven at 100°C and weighed. When catalysts were used, the dichloromethane insoluble material was washed with hot water in an ultrasonic bath. $ZnCl_2$/CuCl remaining in the dicholoromethane insoluble material (except those chemically combined) were thus removed. The solvent was then evaporated in a rotary evaporator (Buchi, Rotavapor RE121). n-Pentane in 1:50 ratio was then added and the mixture placed in an ultrasonic bath for 15 min. It was left for 24 h before n-pentane insolubles, termed as asphaltenes were filtered. The asphaltenes were then dried in a vacuum dessicator, weighed and collected. n-Pentane was evaporated from the filtrate in the rotary evaporator and the remaining yellowish material, termed as maltenes, was collected.

RESULTS

The experimental conditions and product analysis in terms of coke (dichloromethane insolubles), asphaltene (pentane insolubles), maltenes (pentane solubles) and gas are summarized in Table 2. The following observations are made.

The amount of coke and gas increase, in general, with reaction temperature (see expts. 1,5,8 for the non-catalytic and expts. 2,6,9 for the catalytic runs). Both the asphaltene and the maltene fractions appear to decrease with temperature for the range studied (see expts. 1,5,8).

Addition of $ZnCl_2$ decreases the asphaltene, coke and gas fractions whereas it increases the maltene fraction with respect to the uncatalyzed reaction. The asphaltene fraction decreases whereas the maltene fraction increases with increased $ZnCl_2$ as can be seen from expts. 1-4,5-7, and 8-11. The gas fraction initially decreases with respect to the uncatalyzed reaction but increases with additional $ZnCl_2$. Although there is some scatter in the data the coke content also appears to decrease somewhat with $ZnCl_2$.

Addition of tetralin results in decreased gas and coke fractions as can be seen by comparing expts. 1, 12-14. The asphaltene fraction also decreases somewhat whereas the maltene fraction increases. CuCl also has some catalytic activity towards heavy oil cracking, but its reactivity is lower than that of $ZnCl_2$. Addition of CuCl to $ZnCl_2$ lowers the coke content of the product, but decreases the reactivity towards asphaltene cracking as can be seen by comparing expts. 7, 17 and 18.

Some observations on the performance of the bubbling microautoclave with respect to conventional stirred autoclaves are worth mentioning. Our results were compared with those of Herrmann et al. (13), carried out under somewhat similar conditions with Athabasca bitumen. A substantial difference in the quantity of gas formed was noted. In the present case it ranged from 15 to 23 wt % for runs carried out at 440°C and 450°C. In the case of Herrmman et al. (13) it was about 6 wt %. This is probably an indication of improved cracking in the microautoclave. We attribute this to a homogeneous distribution of temperatures and gas throughout the fluidized system and to the absence of hot spots on the walls.

CONCLUSIONS

Athabasca bitumen has been hydrocracked in a bubbling microautoclave with molten halide catalysts. $ZnCl_2$ has been found to be an effective catalyst for the conversion of asphaltenes into maltenes and gases. Since $ZnCl_2$ is in the liquid state under hydrocracking conditions it may be used as a homogeneous catalyst for the hydrocracking of bitumen and heavy oils. The addition of tetralin reduces gas and coke formation but a substantial amount is required to significantly reduce coke.

REFERENCES

1. Pruden, B.B., Canadian J. of Chem. Eng., 56, 277-280, 1978.

2. Nomura, M. Terao, K. and Kikkawa, S., Fuel, 60, 699-702, 1981.

3. Speight, J.G. and Moschopedis, S.E., Fuel Proc. Tech., 2, 295-302, 1979.

4. Chandra Sekhar, M.V. and Ternan, M., Fuel, 58, 92-98, 1979.

5. Pruden, B.B., Logie, R.B. Denis, J.M. and Merrill, W.H., CANMET Report 76-33, 1976.

6. Khulbe, C.P. Pruden, B.B. and Denis, J.M., Laboratory Report ERP/ERL 77-79(J), 1977.

7. Ranganathan, R. Pruden, B.B. and Denis, J.M., CANMET Report 77-62, 1977.

8. Dickie, J.P. and Yen, T.F., Anal. Chem., 39, 1847, 1967.

9. Zeilke, C.W., Struck, R.T., Evans, J.M., Costanza, C.P. and Gorin, E., Ind. Eng. Chem. Process Des. Dev., 5, 158-164, 1966.

10. Nakatsuji, Y., Kubo, T., Nomura, M. and Kikkawa, S., Bul. Chem. Soc. Japan, 51, 618-624, 1978.

11. Nakatsuji, Y., Ikkaku, Y., Nomura, M. and Kikkawa, S., Bul. Chem. Soc. Japan, 51, 3631-3634, 1978.

12. Zeilke, C.W., Klunder, E.B., Maskew, J.T. and Struck, R.T., Ind. Eng. Chem. Process Des. Dev., 19, 85-91, 1980.

13. Herrmann, W.A.O., Mysak, L.P. and Belinko, K., CANMET Report 77-50, 1977.

Table 1

Select properties of Athabasca bitumen

API gravity	10.1		Density	0.999 g/mL
Viscosity, 25°C	42000 cP		Ash	0.48 wt %
Carbon	83.77 wt %		Hydrogen	10.51 wt %
Nitrogen	0.37 wt %		Sulphur	4.75 wt %
Oxygen	0.88 wt %		Vanadium	200 ppm wt
Nickel	75.5 ppm wt		Asphaltene	16.1 wt %
Pitch (524°C+Fraction)	53.7 %		Coke	0.57 wt %
			Maltene	83.33 wt %

Table 2

Summary of the experimental conditions and product analyses

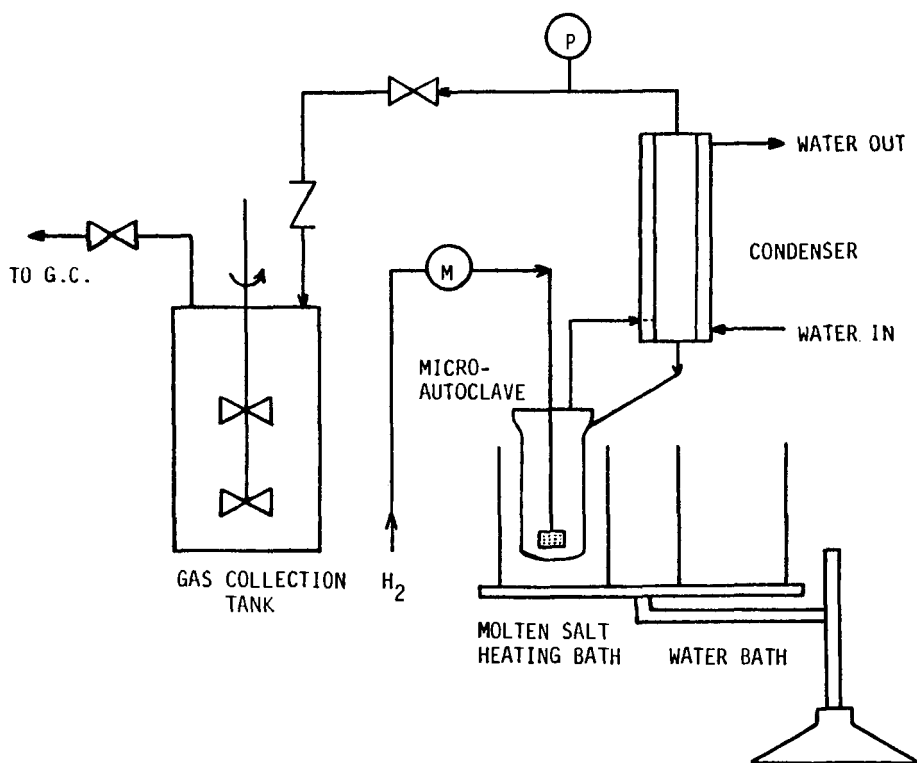| Expt. #	Temp. °C	Catalyst %	Cat. Conc. wt %	Coke wt %	Asphaltene wt %	Maltene wt %	Gas wt %
1	450		-	8.4	8.6	60.1	22.9
2	450	$ZnCl_2$	1.5	5.5	8.2	66.0	20.2
3	450	$ZnCl_2$	10	6.3	4.4	67.7	21.6
4	450	$ZnCl_2$	25	2.8	2.4	72.3	22.5
5	440	-		4.8	10.4	66.7	18.1
6	440	$ZnCl_2$	1.5	3.8	8.3	69.9	18.0
7	440	$ZnCl_2$	10	4.1	3.2	72.1	20.6
8	425	-		3.6	11.7	67.0	17.7
9	425	$ZnCl_2$	1.5	3.2	9.1	74.7	12.9
10	425	$ZnCl_2$	10	4.0	4.7	78.9	12.4
11	425	$ZnCl_2$	25	1.6	4.0	77.7	16.7
12	450	Tetralin	25	4.6	6.5	68.1	20.8
13	450	Tetralin	50	3.8	5.2	73.9	17.1
14	450	Tetralin	100	2.7	5.4	76.5	15.4
15	440	CuCl	1.5	6.7	7.2	67.9	18.2
16	440	CuCl	10	5.9	6.3	69.8	18.0
17	440	$ZnCl_2$+ CuCl	10 1.5	3.6	6.1	70.0	20.3
18	440	$ZnCl_2$+ CuCl	10 4.5	3.4	5.2	72.4	19.0

* values are wt % of feed.

362

Figure 1. Schematic diagram of bubbling microautoclave.